

# **Investigation of Gettering Mechanisms in Crystalline Silicon**

**Final Subcontract Report  
21 July 1997–30 September 2003**

T.Y. Tan  
*Duke University  
Durham, North Carolina*



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NREL Technical Monitor: R. Matson

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## **ABSTRACT**

Accomplishments from research conducted under support of NREL subcontract XAF-7-17607-1 have been reported. Three Ph.D degrees have been granted to students supported by this subcontract, In this investigation, the various aspects of the mechanisms of gettering contaminant impurities away from device active regions in Si have been systematically conducted. Also systematically studied are the modeling of electrical activity of metallic precipitates in Si based on the Schottky effect. With these studies, our knowledge of gettering in Si and on the electrical activity of metallic precipitates in Si has become substantially complete in the sense that interpretations of major experimental results have become self- and mutually consistent.

## SUMMARY REPORT

### 1. PROJECT SUMMARY

The research program supported by NREL XAF-7-17607-1 is entitled *INVESTIGATION OF GETTERING MECHANISMS IN CRYSTALLINE SILICON*. The performance period is from 7/21/1997 to 4/20/2001 (including a nine month extension period from 7/21/2000 to 4/20/2001), and from 9/1/01 to 9/31/03 on a no cost extension basis.

The purpose of conducting the studies supported by this project was to obtain consistent interpretations of existing experimental results, as well as to conduct the needed new experiments, concerning the various phenomena associated with gettering in Si. The investigated gettering method is that by using an Al layer, and the involved works span from studies concerning basic point defect behaviors during gettering to studies of application of the gettering method to improve multicrystalline Si minority carrier diffusion lengths. A preliminary study of the effect of gettering in affecting the solar cell efficiency has been conducted. Moreover, a study of the electrical behavior of precipitated metallic impurities in Si based on the Schottky property of the precipitates, which is a newly proposed physical mechanism, has also been conducted.

As a result of the present studies, our knowledge on such phenomena have become substantially more systematic. This means that interpretations of different experimental results are now largely self- and mutually consistent.

### 2. SUMMARY OF TECHNICAL ACHIEVEMENT

Two outstanding *predictive* simulation results have been obtained under support of the previous subcontract, XD-2-11004-1. The first concerns gettering of pre-introduced Au in Si wafers. For this problem our simulation results indicated that, using an Al layer deposited on *one* side of the wafer, Au will be gettered away from *both* surface regions of the wafer and the gettering effectiveness propagates from both surfaces progressively to greater depths with time. The second concerns the effective of gettering on multicrystalline Si (using Al layers) to

improve the minority carrier lifetimes of the so-called "bad crystal regions" which do not respond to gettering treatment normally employed in the solar cell fabrication process at a temperature below about 900°C for times less than 1 hr. For this problem, our simulation results indicated that a higher temperature will be helpful. Under support of the present subcontract (XAF-7-17607-1), experiments have been conducted to check these predictions. The experimental findings for both cases are positive and appropriate modeling/interpretations are further obtained. In addition to experiments, we have conducted a number of modeling/simulation studies, with all the involved models physically based. These include the void formation process in CZ Si, the optimization of the Al gettering process of bad crystal regions in multicrystalline Si, the electrical property of metallic precipitates in Si, and the influence of gettering on solar cell efficiency. A summary is provided below for each of these accomplishment.

## **2.1. Gettering of Au From Si**

Previous modeling of Al gettering of Au in Si indicated that, for an Al gettering layer placed on one surface of a Si wafer, Au will be gettered from both surface regions of the wafer to progressively greater depths with time. Experimental evidences which confirm the predictions has been obtained. Au was indiffused into a FZ Si wafer at 950°C for 16 hr. After removing the Au source and etching, samples from the indiffused wafer were annealed at 1000°C without or with an Al layer on one surface. For samples without Al, there is no change in the net Au content, while the U-shaped indiffused profile becomes flatter. For samples with an Al layer, both wafer surface region Au concentrations were significantly decreased in 30 min while the wafer interior Au concentrations decreased only after annealing for longer times. A brief physical explanation of the phenomenon is as follows. It is known that Au is a substitutional-interstitial ( $Au_s$ - $Au_i$ ) species with its *indiffusion* governed by the *kick-out mechanism* which is mediated by Si selfinterstitials (*I*). Our previous prediction of the Au gettering process assumes that during gettering by the Al-Si liquid the governing point defect species is also *I*.  $Au_s$  atoms can changeover to  $Au_i$  atoms to rapidly migrate out of Si into the liquid only at the two wafer surface regions, because the consumed *I* will be quickly replenished. In the wafer interior an *I* undersaturation develops which hinders the  $Au_s$ - $Au_i$

changeover and hence the gettering process. The above reasoning is satisfactory in explaining qualitatively why with Al on only one side of the wafer, both wafer surface regions are more effectively gettering than the wafer interior. On a quantitative basis, however, the fit of the data is more satisfactory when it is assumed that during gettering of Au by Al the dominating point defect species is the Si vacancy  $V$  via the *Frank-Turnbull mechanism* instead of  $I$  which dominates under Au indiffusion conditions via the *kick-out mechanism*. For this difference in the Si point defect behavior, an explanation consistent in both thermodynamic and kinetic aspects of the problem has been proposed.

## **2.2. Improvement of Carrier Diffusion Lengths in Multicrystalline Si bad Regions by Al Gettering**

Multicrystalline Si for photovoltaic applications is a very inhomogeneous material with localized regions of high dislocation density and large impurity and precipitate concentrations which limit solar cell efficiency by acting as carrier recombination sites. Due to slow dissolution of precipitates in multicrystalline Si, these regions cannot be improved by conventional P and Al gettering treatments for removal of metal impurities which give good results for single crystal Si. Our previous simulation results showed that an extended high temperature Al gettering treatment can improve minority carrier diffusion lengths in these low quality regions and homogenize the electrical properties of multicrystalline Si wafers. An experiment has conducted in this performance period which showed that this is indeed the case.

## **2.3. Modeling of Void Nucleation and Growth in CZ Si**

In order to reliably model the Au gettering and other processes, we need the point defect parameters  $I$  and  $V$  diffusivity and thermal equilibrium concentration values. Existing data and estimates for the  $I$  diffusivity and thermal equilibrium concentration values are fairly reliable. For  $V$ , however, only the product of the diffusivity and thermal equilibrium concentration is reliable, but not the two values individually. Formation of voids (to sizes of ~100 nm) during large diameter CZ Si crystal growth has provided an opportunity for arriving at these two  $V$



parameters. To this end, we have modeled the nucleation and growth processes of voids under Si vacancy supersaturation conditions. From nucleation barrier calculations, it is shown that voids can be nucleated, but not dislocation loops. The homogeneous nucleation rate of voids has been calculated for different temperatures by assuming different enthalpy of Si vacancy formation. The void growth process has been calculated using a moving boundary formulation. Matching the results of void nucleation and growth simulations and taking into account the competition between the two processes, limited time available, and the crystal cooling rate, it is shown that the experimentally observed void density and size data can be explained if the Si vacancy formation enthalpy is in the range of 2.8 to 3.4 eV and the void nucleation temperature is in the range of 970 to 1060°C.

#### **2.4. A Quantitative Model of the Electrical Activity of Metallic Precipitates in Si**

The multicrystalline Si bad crystal region consists of dislocation entangles upon which many metal silicide precipitates are formed. It is believed that these precipitates are prominent carrier recombination centers which are responsible for the extremely short minority carrier diffusion lengths found in these regions. While the electrical activity metal atoms in Si are fairly well understood, it is somewhat surprising to note that the same is not the case for a metallic precipitate. An inferred origin of the electrical activity is those due to the so-called *interface states* which constitute as charge traps, but measured data indicates that such states cannot account for all the electrical activity of such metallic precipitates. Based on the Schottky property of the precipitate- Si system, we have formulated a quantitative model of the electrical activity of metallic precipitates in Si. In this model, carrier diffusion as well as carrier drift in the Si space charge region are accounted for, and carrier recombination is attributed to the thermionic emission mechanism of charge transport across the Schottky junction rather than surface recombination at traps. It is shown that the minority carrier capture cross-section of the precipitate can be as large as the total capture cross-section of its constituent metal atoms dissolved in the Si matrix. Under weak carrier generation conditions, the supply of minority carriers was found to be the limiting factor of the recombination process. The plausibility of the model is demonstrated by a comparison of calculated and available experimental results.

## **2.5. Variable Temperature Processes for High Gettering Efficiency and Short Needed Gettering Times**

Physical and numerical modeling of impurity gettering from multicrystalline Si for solar cell production has been carried out using Fe as a model impurity. Calculated change of nonradiative recombination coefficient of minority carriers in the course of gettering is used as a tool for evaluating the gettering efficiency. A derivation of the capture cross-section of impurity precipitates, as compared to single atom recombination centers, is presented. Low efficiency of conventional application of gettering process is explained by the modeling results. Variable temperature gettering process is modeled and predicted to provide high gettering efficiency and short needed gettering times.

## **2.6 Gettering and BSF Contributions to Solar Cell Efficiency**

In silicon solar cell fabrication, impurity gettering from Si by an aluminum layer and indiffusion of Al for creating the back surface field (BSF) are inherently carried out in the same process. We have modeled these two processes and analyzed their impact on solar cell efficiency. The output of gettering and Al indiffusion modeling is used as an input for calculation of solar cell efficiency. The cell efficiency gain is obtained as a function of the processes duration. To check the relative contributions of gettering and BSF in improving the cell efficiency, their effects are evaluated together as well as separately. It is found that, for solar cells fabricated from low quality, multicrystalline Si, the efficiency gain is solely due to gettering. In solar cells made of high quality Si, the efficiency gain is primarily due to gettering, but the BSF may play a significant role if the cell thickness is less than about 200  $\mu\text{m}$ . The two effects are found to be synergetic. The model provides a means for optimization of the temperature regime for both processes, as well as for maximization of solar cell efficiency.

## **2.7 Metallic Precipitate Contribution to Generation and Recombination Currents in p-n Junction Devices**

The contribution of metallic precipitates to recombination and to generation currents has been modeled for pn junction devices fabricated using Si, with the precipitate located in the space charge region of the device. The physical mechanism responsible for the electrical activity of the metallic precipitate is attributed to the Schottky junction property between the precipitate and the Si matrix materials. In steady states, it is found that the precipitate changes from a highly effective carrier recombination center to a carrier generation center when the junction bias is changed from forward to reverse biasing conditions. Based on the physical model, numerical simulation results showed that the precipitate electrical behavior resembles that of classical Shockley-Read-Hall (SRH) recombination/generation centers, with a much larger activity.

## **2.8 Metallic Precipitate Contribution to Carrier Generation in Metal-Oxide-Semiconductor Capacitors**

The contribution of metallic precipitates to carrier generation has been modeled for metal-oxide-semiconductor (MOS) capacitor devices fabricated using Si, with the precipitate located in the depletion region of the device. The physical mechanism responsible for the electrical activity of the metallic precipitate is attributed to the Schottky junction property between the precipitate and the Si matrix materials. The precipitate serves as a highly effective carrier generation center when the capacitor is switched from the accumulation mode to the deep depletion mode. As a practical case, the electrical activity of the  $\text{Cu}_3\text{Si}$  precipitate is investigated and the impact of the precipitate located at different positions within the depleted region of the MOS capacitor on the device performance degradation is analyzed.

## **3. STUDENTS**

Under support of this subcontract, three graduate students, Mr. Subhash M Joshi, Mr. Pavel S. Plekhanov, and Mr. Mihai D. Negoita, have received P.h. D. Degrees respectively in

May, 2000; December, 2000; and May, 2003. Mr. Joshi's Ph. D. dissertation title is *ALUMINUM GETTERING OF CRYSTALLINE SILICON FOR IMPROVEMENT OF MINORITY CARRIER DIFFUSION LENGTH AND FOR STUDIES OF FUNDAMENTAL DIFFUSION MECHANISMS*. Mr. Plekhanov's Ph. D. dissertation title is *DEFECTS AND GETTERING OF IMPURITIES IN SILICON*. Mr. Negoita's Ph. D. dissertation title is *METALLIC PRECIPITATE CONTRIBUTION TO GENERATION AND RECOMBINATION CURRENTS IN  $pn$  JUNCTION DEVICES AND IN MOS CAPACITORS VIA THE SCHOTTKY EFFECT*.

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2. P. Plekhanov, and U. M. Gösele, and T. Y. Tan "Modeling of Nucleation and Growth of Voids in Silicon" *J. Appl. Phys.* 84, 718 (1998).
3. P. S. Plekhanov, R. Gafiteanu, U. M. Gösele, and T. Y. Tan, "Modeling of Gettering of Precipitated Impurities for Carrier Lifetime Improvement in Solar Cell Applications", *J. Appl. Phys.* 86, 2453-2458 (1999).
4. P. S. Plekhanov and T. Y. Tan, "A Schottky Effect Model of Electrical Activity of Metallic Precipitates in silicon" *Appl. Phys. Lett.* 76, 3777-3779 (2000).
5. S. M. Joshi, U. M. Gösele, and T. Y. Tan, "Extended high temperature Al gettering for improvement and homogenization of minority carrier diffusion lengths in multicrystalline Si", *Solar Energy Materials and Solar Cells*, in press (2001).
6. P. S. Plekhanov, M. D. Negoita, and T.Y. Tan, "Effect of Al-induced gettering and back surface field on the efficiency of Si solar cells" (2001). *J. Appl. Phys.* 90, 5388 (2001).
7. M. D. Negoita and T.Y. Tan, "Metallic Precipitate Contribution to Generation and Recombination Currents in p-n Junction Devices" *J. Appl. Phys.* (Nov. 1, 2003).
8. M. D. Negoita and T.Y. Tan, "Metallic Precipitate Contribution to Carrier Generation in MOS Capacitors due to the Schottky Effect" *J. Appl. Phys.* (Jan. 1, 2004).

#### 4.2. REFERRED CONFERENCE PROCEEDING AND HANDBOOK PUBLICATIONS:

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5. Teh Y. Tan and Pavel S. Plekhanov, "A Quantitative Model of the Electrical Activity of Metal Silicide Precipitates in Silicon Based on the Schottky Effect" in *Si Front-End Processing-Physics and Technology of Dopant-Defect Interactions III*, eds. E. C. Jones, K. S. Jones, M. D. Giles, P. Stolk, and J. Matsuo, Proc. of Mater. Res. Soc. 669 (Mater. Res. Soc., Pittsburgh, PA, 2001) p. J6.11-16.
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8. T. Y. Tan, "Impurity Gettering in Silicon" in *Encyclopedia of Materials: Science and Technology*, ed. Subhash Mahajan (Elsevier, Amsterdam, 2001) pp. 4031-4042.

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2. P. S. Plekhanov, U. M. Gösele, and T. Y. Tan, "Improvement of carrier lifetime in silicon by gettering of precipitated impurities", in *Extended Abstracts and Papers of the*

Eighth workshop on Crystalline Silicon Solar Cell Materials and Processes, p. 211-214 (1998).

3. T.Y. Tan and P. S. Plekhanov, "Effects of Al-Gettering and Al-Indiffusion Induced Back-Side-Field on the Efficiency of Si Solar Cells", in Extended Abstracts and Papers of the Ninth workshop on Crystalline Silicon Solar Cell Materials and Processes, p. 46-49 (1999).
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13. ABSTRACT (Maximum 200 words): In this investigation, various aspects of the mechanisms of gettering contaminant impurities away from device active regions in Si have been systematically conducted. Also systematically studied are the modeling of electrical activity of metallic precipitates in Si based on the Schottky effect. With these studies, our knowledge of gettering in Si and on the electrical activity of metallic precipitates in Si has become substantially complete in the sense that interpretations of major experimental results have become self- and mutually consistent. The purpose of conducting the studies supported by this project was to obtain consistent interpretations of existing experimental results, as well as to conduct the needed new experiments, concerning the various phenomena associated with gettering in Si. The investigated gettering method is that by using an Al layer, and the involved works span from studies concerning basic point defect behaviors during gettering to studies of application of the gettering method to improve multicrystalline Si minority-carrier diffusion lengths. A preliminary study of the effect of gettering in affecting the solar cell efficiency has been conducted. Moreover, a study of the electrical behavior of precipitated metallic impurities in Si based on the Schottky property of the precipitates, which is a newly proposed physical mechanism, has also been conducted. As a result of the present studies, our knowledge on such phenomena have become substantially more systematic.				
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